but the experiments have led to concordant results for the mass of this carrier. In free space the mass of the electron may be taken as 1/1845 times that of the hydrogen atom, while we have found for the carrier in copper 1/1660, in aluminium 1/1590, and in silver 1/1540. We hope to construct a new apparatus which will increase the accuracy of measurement enough so that we can make certain whether the mass of the carrier is really larger in metals than in free space.

A more complete account of these experiments has been accepted by the *Physical Review* for publication.

THE SILVER VOLTAMETER AS AN INTERNATIONAL STANDARD FOR THE MEASUREMENT OF ELECTRIC CURRENT

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The International Electrical Conference which met in London in 1908 adopted the ampere as the second fundamental electrical unit, the ohm being the first, and defined the international ampere in terms of the electrolytic deposit of silver in the silver voltameter. At the time of this conference it was the opinion of the delegates from this country that the volt should have been chosen in place of the ampere, because the standard cell was more reproducible than the silver voltameter and was the means then as now actually employed (in conjunction with the ohm) for measuring the ampere by the drop in potential method. The decision of the conference was, however, accepted as final, and researches were undertaken in several different countries, and particularly in this country, with the aim of making the voltameter worthy to bear the responsibility imposed upon it by the London Conference. The purpose of this paper is to give briefly the most important results that have been obtained and to show the remarkable agreement of the measurements recently made in the national laboratories of several different countries of the electromotive force of a Weston normal cell, in terms of the international volt as officially defined. This agreement is due to the fact that great advances have been made in our knowledge of the silver voltameter in recent years; and although no adequate specifications have been formally adopted, the methods followed by recent investigators have agreed in essential particulars, although differing in details.

No concrete standard for the ampere, corresponding to the column

of mercury for the ohm or the standard cell for the volt, is possible. The value of an electric current may, however, be conveniently expressed for the purposes of precise measurement in two ways. Either the silver voltameter may be used to calibrate an ampere balance as was done by the British Board of Trade, or the voltage of the Weston normal cell may be determined when a measured current passes through a known resistance. The latter method was adopted by the London Conference, but at that time information was lacking as to the proper value to assign to this cell, which was adopted by the conference in place of the Clark cell.

In 1910 a committee consisting of representatives of the National Laboratories of England, France, Germany, and the United States met in Washington and made careful voltameter measurements to determine the voltage of the Weston normal cell, in the manner agreed upon at London in 1908. The Committee found the value to be very nearly 1.0183 volts at 20°C. This value, recommended by the Committee as the international value of the Weston normal cell, has become the basis of measurement in general use for voltage and (with a resistance) for current measurements also. Although the cell has thus become the practical standard, the voltameter has not lost its importance, for it is the ultimate standard which is to be depended upon in the future to determine whether the standard cells preserved by the various national laboratories are maintaining an unchanging voltage.

The researches on the voltameter which have been made since the international technical committee adjourned have been in part for the purpose of finding out with greater precision (to the sixth significant figure) how close the value for the cell as computed from the voltameter results and the international ohm is to the value 1.0183 volts adopted by the Committee. Although the difference is inappreciable for most purposes, it is desirable that it be determined as accurately as possible. It is also very necessary to have adequate specifications for the voltameter that shall enable us to obtain results in the future comparable with those obtained now. In this work the Bureau of Standards has been able to take an active part. Many sources of error in the voltameter have been discovered and means for their elimination provided, and the voltameter may now be considered capable of being used to check the voltage of the Weston normal cell.

During the course of the work differences of opinion have arisen among some of the investigators in this and other countries, but by co-operative experiments and correspondence practically all of these differences

have been settled so that at present, we believe no important questions are still outstanding. A few of the most important developments during the recent voltameter work may be mentioned.

It was well known before the Bureau of Standards began its work that the deposits in the Rayleigh or filter-paper form of voltameter exceeded those in the porous cup voltameters which were used in series with them. No satisfactory explanation of this difference had been given, and its existence had indeed been questioned. The most recent investigation prior to the London Conference appeared to show that under certain conditions the two forms of voltameter agreed. It was discovered at the Bureau of Standards that the difference could be doubled if the amount of filter paper was doubled and that when the filter paper was wrapped around the porous cup the results were the same as if the porous cup were not present. In short, it was definitely proved that the filter paper itself was a source of serious error in the voltameter. A chemical study showed that the cellulose fibers of the filter paper are slightly oxidized in the air and the minute amounts of oxycellulose are soluble in water. These give rise to strong reducing agents in silver nitrate solutions and colloidal silver is formed. The colloidal particles carry electrical charges much smaller proportionally to their mass than do the univalent silver ions and therefore give rise to deposits in excess of the true deposit according to Faraday's law. They also alter the form and appearance of the deposit.

Methods have been developed at the Bureau for the preparation and testing of silver nitrate of the exceptional purity which is necessary for voltameter work, because very minute impurities produce exaggerated effects in the voltameter deposits. All forms of voltameter (except the filter paper form and forms using linen, cotton, silk, etc., as a septum) are in substantial agreement when used with solutions of the highest purity and with proper precautions against anode slime. The temperature coefficient with pure solutions was shown to be zero as it ought to be. The precaution taken by some observers to soak the silver deposits over night in distilled water to remove the last traces of electrolyte was shown to be harmful because it was discovered that silver in contact with platinum is appreciably soluble in distilled water. This was shown by repeated tests. The silver and the platinum differ slightly in potential so that a current passes from the silver to the platinum through the water. Although this current is very small, it was demonstrated by a sensitive galvanometer and the loss of silver from the deposit was measured.

Another discovery of importance is the alloying effect of the silver and platinum when determining the inclusions of foreign matter in the deposits by the method of heating. After the slight alloying has taken place, the removal of the silver leaves a very thin layer of platinum black on the inside surface of the cup. Unless this is entirely removed its adsorptive properties make the weight of the cup uncertain and its catalytic properties cause the deposition of hydrogen ions when another silver deposit is made so that the amount of silver is not a true measure of the electricity according to Faraday's law.

Various observers in different countries by avoiding these sources of error have obtained very concordant results as the following table shows:

TABLE 1

VALUES FOR THE WESTON NORMAL CELL AT 20°C. COMPUTED FROM SILVER VOLTAMETER MEASUREMENTS

COUNTRY*	FORM OF VOLTAMETER†	VALUE FOR CELL	Δ
			parts in 100 000
United States	Smith	1.01827_4	-0_2
United States	Richards	1.01826_7	-0_9
Japan	Smith	1.01826_9	-0_7
Russia‡	Smith	1.01829_5	$+1_9$
Holland	Smith	1.01826	-1_6
Germany	Kohlrausch	1.01829_0	$+1_4$
Mean		1.01827_6	$\pm 1_1$

* England and France have not published any measurements of this kind since the time of the International Committee. The Observers are: for Japan, Obata; for the U. S., Rosa, Vinal, and McDaniel; for Russia, Mlle. Ferringer; for Holland, Haga and Boerema; for Germany, von Steinwehr.

† The Smith form and the Kohlrausch form are similar in principle. They have no separation between anode and cathode except a glass trap to catch the anode slime, but the construction of this trap is very different in the two forms. The Richards form makes use of a porous cup septum.

‡ This is the mean of four sets of measurements on a particular cell at different periods during several years.

The average deviation from the mean result is only 0.001%. The experimental error involves the errors of both the cell and the standard resistance as well as the numerous sources of error in the voltameter itself. These include the errors of weighing the bowls both before and after the deposit, the errors of timing the deposits, the errors due to fluctuation in the current, and the errors in washing and drying the deposits. In view of these it is remarkable how small the deviations are for the individual countries. These results are the work of investigators

of five nationalities using three different types of instruments, and yet they agree to about 1 part in 100,000.

The national laboratories were in correspondence on the matter of specifications when the war in Europe began. Since then the Bureau of Standards has prepared and published its specifications for the voltameter and it will recommend these for adoption when it is again possible to do so after the restoration of peace.

The specifications which the Bureau of Standards has formulated have been made as broad as is consistent with work of the highest accuracy. They do not specify any particular form of voltameter, but rather the conditions which must be fulfilled by the voltameter. The concentration of the solution is given rather wide limits because it has been found that identical results may be obtained with pure solutions over a considerable range.

An important question as to the purity of the silver obtained has only recently been settled. The impurities are very small, as indeed previous observers, including Van Dijk in Holland, Jaeger and von Steinwehr in Germany, and Boltzmann in Austria, have previously shown. The Bureau of Standards has found the average amount of foreign matter in its standard deposits to be about 0.004%. It is so uniform in the different deposits that the results given by the voltameter as a measuring standard are sufficiently accurate without the necessity of determining the foreign matter in each individual deposit. Without the greatest precautions the error introduced in attempting to determine the inclusions will be greater than the total amount of the inclusions.

In some of the experiments at the Bureau of Standards our absolute current balance has been used in connection with the silver voltameter. This has permitted the determination of the absolute electrochemical equivalent of silver. It was found to be 1.11804 mg. per coulomb, but when corrected for the inclusion of foreign material this becomes 1.11800 mg. This figure is exactly the value assigned to this constant, although at the time it was adopted by the London Conference, eight years ago, the best information available indicated a higher value by about 30 parts in 100,000. In Holland, Prof. Haga, has obtained 1.11802 using a tangent galvanometer. We believe that the closest figure that can be assigned at the present time to this constant is the round number 1.11800 mg. per absolute coulomb, and is this precisely the value fixed by international agreement in 'international coulombs.'

Since one absolute coulomb of electricity deposits 0.00111800 gram of silver, the number required to deposit a gram-equivalent of silver,

107.88 grams, is 96,494 coulombs, which is the value of the Faraday. For general use the value 96,500 coulombs is a convenient round number which is within the experimental error.

Although some phenomena of the voltameter are not yet perfectly understood, the recent researches have shown how to use it as a reliable current standard and as a means of checking the constancy of the value of the Weston normal cell. The experiments made at the Bureau of Standards during the past eight years have been fully described in a series of papers which have appeared in the *Bulletin* of the Bureau.